ORGANIC ELECTROLUMINESCENCE GENERATING DEVICES

Field of the Invention

The present invention is related to the field of organic and polymer electronics, more specifically it is related to the field of organic light-emitting devices.

Background of the Invention

Organic electroluminescence generating devices are typically fabricated by sandwiching one or more organic layers between conductive electrodes. Upon application of an electric field, negative charges are injected into the organic layer or organic layers from one electrode, and positive charges are injected into the organic layer or organic layers from the other electrode. Injected charges travel across the organic layer or organic layers until when they radiatively recombine to emit light.

Examples of prior art organic electroluminescence generating devices are vertical stacks of organic layers sandwiched between two electrodes as illustrated in figure 1. An alternate example of prior art organic electroluminescence generating devices comprises three electrode devices where conductive electrodes injecting negative and positive charges into the organic layers are vertically displaced and separated by one or more organic layers. Injected charges travel across the vertical stack of organic layers until they radiatively recombine to emit light. An illustrative example of such structure is shown in figure 2.

The vertical displacement of the charge injecting electrodes requires that charge carriers travel across organic layers thereby limiting charge carriers mobility. It is known in the art that charge carrier mobilities in most organic thin films are significantly higher in a plane parallel to the substrate than in a direction perpendicular to the substrate, when these planes correspond to deposited organic layers.

Aim of the Invention

An aim of the present invention is to provide novel

electroluminescence generating devices which advantageously combines charge carriers mobility occurring in a plane parallel to the substrate, thereby taking full advantage of the higher in-plane charge carriers mobility, simplified device fabrication with simultaneous fabrication of charge injecting electrodes, and electrical characteristics controlled by the controlling electrode.

This aim and other aims that will become apparent from the following disclosure are reached by the electroluminescence generating devices of the present invention, comprising a thin layer, that is further referred to as the channel, comprising at least one layer of an organic semiconductor, and three or more electrodes. At least one electrode is suitable for injecting one type of charge carriers (e.g. holes), at least one electrode is suitable for injecting the other type of charge carriers (e.g. electrons) and at least one electrode, that will be referred to as the controlling electrode, is suitable to control the charge injection and/or the charge recombination within the channel and/or the current flow between at least two of the above electrodes. The electrodes for_injecting one type of charge carriers (e.g. holes) into the channel and the electrodes for injecting the other type of charge carriers (e.g. electrons) into the channel are preferrably positioned in an essentially horizontal plane along the channel. The controlling electrode is preferably separated from the organic semiconductor by a dielectric layer. The injected charge carriers of opposite sign recombine radiatively to generate light. An illustrative view of a light-emitting device of the present invention is illustrated in Figure 3.

<u>Summary of the Invention</u>

The present invention provides an electroluminescence generating device comprising:

a. a channel of organic semiconductor material, the channel being able to carry both types of charge carriers, the charge carriers being electrons and holes;

b. an electron electrode, the electron electrode being in contact with the channel and positioned on top of a first side of the channel layer or within the channel layer, the electron electrode being able to inject electrons in the channel layer;

c. a hole electrode, the hole electrode being spaced apart from the electron electrode, the hole electrode being in contact with the channel and positioned on top of the first side of the channel layer or within the channel layer, the hole electrode being able to inject holes into the channel;

d. a control electrode positioned on the first side or on a second side of the channel;

whereby light emission of the electroluminescence generating device can be acquired by applying an electrical potential difference between the electron electrode and the hole electrode.

Advantageously the electroluminescence generating device comprises further a dielectric layer between the channel and the control electrode.

This dielectric layer preferrably comprises at least one material selected from the group consisting of silicon oxide, alumina, polyimide and polymethylmetacrylate

In preferred embodiments at least one of the electron electrode and the hole electrode comprises at least one different material which is not comprised in the other one.

The electron electrode preferably comprises one or more elements selected from the group consisting of Au, Ca, Mg, Al, In, Perovskite Manganites ($Re_{1-x}A_xMnO_3$).

Preferably the hole electrode comprises at least one material selected from the group consisting of Au, indium tin oxide, Cr, Cu, Fe, Ag, poly(3,4-ethylenedioxythiophene) combined with poly(styrene sulfonate), Perovskite Manganites ($Re_{1-x}A_xMnO_3$).

The channel can comprise at least one material selected from the group

consisting of small molecule materials, polymers and metal complexes.

Advantageously the channel comprises at least one material selected from the group consisting of tetracene, pentacene, perylenes, terthiophene, tetrathiophene, quinquethiophene, sexithiophene, bora-diazaindacene, polyphenylenevinylene, polyfluorene, polythiophene and porphyrins.

In certain embodiments according to the present invention, the channel comprises an amorphous semiconductor material

In other embodiments the channel comprises a poly-crystalline semiconductor material

In advantageous embodiments, the channel comprising poly-crystalline semiconductor material has a crystal grain size and the hole electrode and the electron electrode are spaced apart at a distance smaller then the grain size.

Advantageously the hole electrode and the electron electrode are spaced apart at a distance between 5 nm and 5 microns.

In certain embodiments according to the present invention, leading to higher light-output per device, electron electrode and the hole electrode have digitated structures comprising a regular repetition of a basic finger structure, and are positioned such that the basic finger structures of respectively hole and electron electrodes are alternating each other, and is characterised by two in-plane distances P and R between the basic finger structures.

Advantageously the distances P and R are equal.

In certain embodiments the control electrode is an injection control electrode, the injection control electrode being positioned on the second side of the channel, whereby the application of an electrical potential difference between the control electrode and the hole electrode or electron electrode, facilitates the injection of charge carriers into the channel.

In other embodiments the control electrode is a current control electrode, the current control electrode being positioned on the second side of the channel, whereby the application of an electrical potential difference between the control electrode and the electron and/or hole electrode allows to

control the current of at least one type of charge carriers.

The channel can comprise more then one sublayers.

In certain embodiments, the channel comprises an electron injection type sublayer, able to facilitate injection of electrons, a hole injection type sublayer, able to facilitate injection of holes, and a recombination type sublayer, able to facilitate recombination of the charge carriers.

The devices according to the present invention can further comprise optical confinement and/or waveguiding layers on the first and/or the second side of the channel.

The devices according to the present invention can further comprise optical resonating structures or cavities on the first and/or the second side of the channel.

The devices according to this invention can comprise a flexible or rigid substrate.

The channel can be formed by sublimation of small molecules.

The channel can be formed by simultaneous sublimation of at least two moieties.

The channel can also be formed by solution processing of one or more soluble and/or polymeric materials.

The channel can also be formed by a combination of sublimation and solution processing

This channel can be formed by thermal, chemical or physical treatment of pre-deposited organic semiconductors.

It can also be manufactured with printing techniques.

The devices according to the present invention make optimal use of a method for generating electroluminescence, by recombination of electrons and holes injected in the channel from the electron electrode and hole electrode.

They advantageously combine the fact of higher charge carrier mobilities when occurring in a plane parallel to the substrate. The devices

are easy to fabricate. At least one controlling electrode is present to control the electrical and light-emission characteristics of the light-emitting device.

Brief Description of Drawings:

Figure 1 is a cross section view of a prior art light-emitting device with two electrodes, wherein A is a cathode electrode, B is an organic light-emitting layer, C is an organic semiconductor layer, D is a hole injection layer, E is an anode electrode and F is a glass substrate.

Figure 2 is a cross section view of a prior art light-emitting device with three electrodes, wherein G is a cathode electrode, H is an organic light-emitting layer, I is an organic semiconductor transport layer, L is a source electrode, M is a gate dielectric layer, N is a transparent gate electrode and O is a glass substrate.

Figure 3 is a cross section view of an electroluminescence generating device of the present invention, wherein 1 is a substrate, 2 is a controlling electrode, 3 is a dielectric layer, 4 is a channel comprising layers of organic semiconductors, 5 is a hole injecting electrodes, 6 is an electron injecting electrodes, 7 is electroluminescence.

Figure 4 is a graph illustrating the current between electrodes 5 and 6 and the corresponding generated electroluminescence as a function of the voltage between electrodes 5 and 6 for a constant voltage between electrodes 2 and 6 of the electroluminescence generating device of Figure 3 in the case when the current of one type of charge carriers (holes in Figure 4) dominates over the current of the other type of charge carriers (electrons in Figure 4).

Figure 5 is a graph illustrating the current between electrodes 5 and 6 and the corresponding generated electroluminescence as a function of the voltage between electrodes 2 and 6 for a constant voltage between electrodes 5 and 6 of the electroluminescence generating device of Figure 3 in the case when the current of one type of charge carriers (holes in Figure 5) dominates over the current of the other type of charge carriers (electrons in Figure 5).

Figure 6 is a graph illustrating the current between electrodes 5 and 6

(Top) and the corresponding generated electroluminescence (Bottom) as a function of the voltage between electrodes 5 and 6 for a constant voltage between electrodes 2 and 6 of the electroluminescence generating device of Figure 3 in the case when the device is operated in ambipolar mode, i.e. simultaneous p- and n-channels are formed. For negative bias between electrodes 2 and 6, typical p-channel characteristics are observed when the bias between electrodes 5 and 6 is negative and the absolute value of the voltage between electrodes 5 and 6 is smaller or equal to the absolute value of the voltage between electrodes 2 and 6. Increasing the absolute value of the voltage between electrodes 5 and 6, the current between electrodes 5 and 6 increases due to electron injection in the device and ambipolar operation. Similarly, for positive bias between electrodes 2 and 6, typical n-channel characteristics are observed when the bias between electrodes 5 and 6 is positive and the value of the voltage between electrodes 5 and 6 is smaller or equal to the value of the voltage between electrodes 2 and 6. Increasing the value of the voltage between electrodes 5 and 6, the current between electrodes 5 and 6 increases due to hole injection in the device and ambipolar operation.

Figure 7 is a photograph of the top view of an electroluminescent device according to the present invention, showing electrode fingers. Fingers '5' are the hole-injecting electrodes of Figure 3, and are made of Au. Fingers '6' are the electron-injecting electrodes of Figure 3 and are made of Ca. In the area in between the fingers is the electroluminescent organic material. The controlling electrode '2' of Figure 3 is not visible in Figure 7, as it is covered by a gate dielectric and by the structures visible in the photograph.

Figure 8 is a photograph similar to Figure 7 but with a larger magnification, showing Au fingers '5' and Ca fingers '6', with tetracene organic material in the channel between the finger contacts.

Figure 9.a is a detail picture of an alternating interdigitized structure

of calcium and gold contacts. The organic semiconductor material on top of these contacts is tetracene. Figure 9.b is the negative image of light-emission from the tetracene layer in this structure when the contacts are voltage-biased according to the measurement shown in Figure 11.

Figure 10 represents a measurement on a device structure with alternating gold and calcium injection contacts deposited on the silicon oxide surface layer of a silicon substrate. The silicon substrate is metallized with aluminum, which serves as a controlling electrode. The electrode numbering is according to the one used in Figure 3.

Figure 11 is a schematic representation of a possible injection mechanism of electrons from an injecting electrode to an organic layer, driven by the voltage applied between electrodes 5 and 6 of Figure 3. The large electric field at the injecting contact induces a local distortion of the organic material electronic levels (Lowest Unoccupied Molecular Orbital (LUMO) (8) and Highest Occupied Molecular Orbital (HOMO) (9) levels) that facilitates charge carriers injection (electrons (e^-) in Figure 11) via a tunneling process from the Fermi level (E_F) of the injecting electrode to the level 8 of the organic material.

Modes for Carrying out the Invention

In a preferred embodiment the device has three electrodes. A first electrode is suitable for injecting one type of charge carriers (e.g. holes), a second electrode is suitable for injecting the other type of charge carriers (e.g. electrons) and a third controlling electrode is suitable to control the charge injection, the charge recombination and the current flow between the first and the second electrodes. The controlling electrode is preferably separated from the semiconductor by a dielectric layer. The injected charge carriers of opposite sign recombine radiatively to generate light.

In another embodiment the device has at least two controlling electrodes. In one embodiment one controlling electrode can be used to control the current flow of one type of charge carriers and another

controlling electrode can be used to control the current flow of the other type of charge carriers.

In another embodiment one controlling electrode is used to control the injection of one type of the charge carriers and a second controlling electrode is used to control the injection of the other type of the charge carriers.

In another embodiment one controlling electrode is used to control the spatial distribution of one type of the injected charge carriers and a second controlling electrode is used to control the spatial distribution of the other type of the injected charge carriers.

In another embodiment one controlling electrode is used to control the current flows and a second controlling electrode is used to control the location of the charge carrier recombination zone within the organic semiconductor layer.

A controlling electrode can be used to control the injection of a type of charge carriers.

In another embodiment the electrodes which act as carrier injection electrode can be integrated in an interdigitated structure where one type of electrode, which injects one type of carriers, is alternated in space with the electrode which injects the opposed type of carriers. A purely illustrative example of such structure is represented in Figure 7, where gold and calcium electrodes are alternatingly repeated. The device in Figure 7 consists of a silicon substrate with silicon oxide on top. In a first step of a process for manufacturing such a device, the gold electrodes are vacuum deposited by metal evaporation through a shadow mask. Secondly, the calcium electrodes are deposited similarly through another shadow mask. Then a tetracene layer is deposited by vacuum deposition. The aluminum metal on the backside of the silicon substrate serves as controlling electrode. The carrier injection electrodes (here gold and calcium) can be situated beneath an active organic layer or above it. The performance of such device in terms of charge carrier

transport and light-emission will be optimized if the distances from one type of electrode to its two electrodes adjacent (given by P and R in Figure 8) are equal.

The injection of electrons and holes in the above structure is important for the functioning of the device. Injection of charge carriers can be mediated by impurities and hetero-species. Impurities and hetero-species can act to form a staircase of energy levels that facilitate charge injection into the channel. The incorporation in the channel of impurities and hetero-species can therefore be used to facilitate the injection of one or both types of charge carriers. Examples of impurities are atoms, ions, molecules different from the main moiety of the channel. Also doping atoms or molecules can be used as such impurities. Prior art shows that doping atoms or molecules introduced in a semiconductor undergo an ionisation process and leave a charged particle (atom or molecule) that changes the potential distribution, which effect can be used to facilitate injection of a type of carriers into a semiconductor.

Other means to facilitate charge carrier injection include the use of a large electric field at the injecting contact. Such favourable field can be created for instance by the electrode configuration, by the electrode shape, by the creation of an accumulation of charge carriers. A schematic representation of the possible role of the electric field in assisting charge carrier injection is shown in Figure 11.

Charge carrier injection can also be facilitated by the use of a material for the injecting electrode that has a low barrier against injection of a charge carrier type in a channel of the device. Examples of materials that can be used to fabricate the injecting electrodes are Au, Ca, Mg, Al, In, Perovskite Manganites ($Re_{1-x}A_xMnO_3$), indium tin oxide, Cr, Cu, Fe, Ag and poly(3,4-ethylenedioxythiophene) combined with poly(styrene sulfonate). Charge carrier injection into the channel can further be facilitated by interposing one or several layers of material that form a staircase of electronic levels

between the energy level of the injecting electrode and the energy level required for injection in a semiconductor.

Charge carrier injection and electroluminescence can also be facilitated by designing the injection electrodes to fit the morphology of an organic material which is used as active layer. The morphology is determined by the intrinsic property of the organic materials and the deposition method. The distance between the injection electrodes can be smaller than the average grain size of poly-crystalline films (typically in the range of 20 nanometers to 5 micrometers). In such case, carriers of opposite type (electrons and holes) can be injected in one grain by the electrodes '5' and '6' directly into a single grain of the poly-crystalline organic semiconductor. As an example, Figure 9 shows a gold metal and calcium electrode adjacent to each other with a distance of less than one micrometer between them. This list of methods to facilitate injection of charge carriers is not intended to be limitative, and a person skilled in the art can extend it to more methods.

An aim of this embodiment of the invention is to provide an electroluminescence generating device comprising a channel having at least one layer of an organic semiconductor, at least two electrodes for injecting two different types of charge carriers, and at least one controlling electrode, and a method to facilitate the injection of at least one type of charge carriers into the channel. The channel of the device of the present invention consists of at least one layer of organic semiconductor. An organic semiconductor can consist of small molecules (whereby it is meant molecules that can be processed by sublimation), preferably tetracene, pentacene, perylenes, oligothiophens (terthiophenes, tetrathiophene, quinquethiophene or sexithiophene), bora-diazaindacene fluorophores; it can be a polymer, such as polyphenylenevinylene, polyfluorene or polythiophene; it can be a metal complex such as Pt-octaethylporphyrin. The list of materials is not intended to be limitative, but only to provide examples. The organic semiconductor

used in the channel can consist of small molecules and polymers, which have been chemically, electrochemically or physically processed to show n-type (or alternatively p-type) behavior in combination or in place of the p-type (or alternatively n-type) transport characteristics.

In another embodiment, the channel can consist of several layers of organic semiconductors, each of them with a specific function in the device. In an embodiment the channel consists of two layers of organic semiconductors. In one layer of organic semiconductor the injection and transport of one type of charge carriers preferentially occurs, in the other layer of organic semiconductor the injection and transport of the other type of charge carriers preferentially occurs. Charges of opposite sign recombine radiatively in one of the two layers of organic semiconductors or at the interface between them to generate light.

In another embodiment the channel consists of three layers of organic semiconductors. In one layer of organic semiconductor the injection and transport of one type of charge carriers preferentially occurs, in another layer of organic semiconductor the injection and transport of the other type of charge carriers preferentially occurs. In the third layer of organic semiconductor or at one of the interfaces between the third and the other two layers the charges of opposite sign recombine radiatively to generate light.

Organic layers or doping moieties can be inserted in the channel to facilitate and optimize light emission via, for example, energy transfer processes from the organic species in which the charges first recombine to the organic layers or doping moieties which act as energy acceptors. The energy transfer process can be used to separate zones within the channel with high electric fields and high density of free carriers from the zone where exciton recombination and light emission occurs, which would result in improved light emission efficiency of the device.

In another embodiment the channel consist of a co-evaporated layer of two or more materials. The materials may have specific charge transport,

charge recombination, energy transfer and light emission functions in the device.

In another embodiment the channel consist of two co-evaporated materials, each acting as a transport mean for one type of charge carriers in the channel. One type of charge carrier is injected in one material which is in contact with an injecting electrode and is transported via an interpenetrated path towards the other electrode. The other type of charge carrier is injected by the other electrode in the other material and is transported via an interpenetrated path towards the other electrode. The two types of charges recombine in the channel and generate light emission.

In another embodiment the channel is formed by solution processing a polymer or a polymer blend that creates an interpenetrating network of p-type and n-type materials.

The channel can further be realized by several coplanar layers of organic semiconductors, each of them with a specific function (charge injection, charge transport, charge recombination, energy transfer and light emission, just to mention some possible functions) in the device.

The channel can also be realized by a combination of coplanar layers of organic semiconductors and vertically stacked layers of organic semiconductors.

Transport of a type of charge carriers through the entire channel may not be necessary, provided that injected charges into the channel recombine radiatively with charges of opposite sign to emit light.

Examples of materials for injecting electrodes are gold, calcium, aluminium, magnesium. Examples of dielectrics are silicon dioxide (also in its porous form), alumina, polyimide, polymethylmetacrylate. The list of materials is not intended to be limitative, but only to provide examples.

In a further improvement of the device, optical confinement layers are added to the device structure below and/or above the channel. Preferred means of optical confinement comprise a structure of material with lower

refractive index than that of the channel, such as to provide optical confinement by waveguiding, and a reflector, such as a distributed Bragg reflector or a metal mirror.

Depending on the channel characteristics, on the materials used and on the optical confinement layers, light can be emitted isotropically or in specific directions or within a specific solid angle.

The device according to the invention can be made in different configurations. In a first configuration, a controlling electrode or controlling electrodes are deposited first on a substrate, followed by a dielectric, followed by injecting electrodes, followed by a channel layer that comprises an organic semiconductor. In an alternative embodiment, an injecting electrode is deposited on top of a channel, as shown in Figure 3. In yet another embodiment, a dielectric and a controlling electrodes are deposited on top of a channel.

The devices according to the invention are operated by applying a first appropriate bias voltage to a controlling electrode, and injecting electrons from a first electrode and holes from a second electrode, while maintaining a second bias voltage between the latter two electrodes. The first and second bias voltages can be continuous voltages. In an alternative operation method, they can also be pulsed voltages. The devices can be operated at room temperature. In alternative, they can be operated in the temperature range from 1°Kelvin to 450°Kelvin.

The light output of the device can be perpendicular to the plane of the substrate and the layer sequel described above. It can also be guided in the plane of the substrate, in particular when optical confinement layers as described above are provided. The light output can be incoherent.

The light output can also be coherent and light output can be laser emission. In an embodiment of lasers based on the above described device structure suitable organic semiconductors, optical confinement structures, optical resonators or cavities are used so to provide coherent light output and

lasing.

The device structure of the present invention is compatible with planar technology and can easily be integrated into electronic and optoelectronic Integrated Circuits. The potential of nanotechnology, in particular for down-scaling the relevant device features and for nanostructuring the channel, can be used to optimize and tailor the device characteristics.

The use of the above mentioned devices range from nanoscale light sources for nanophotonics and nano-optoelectronics, optoelectronic Integrated Circuits, lasers applications, displays, information technologies, ambient and automotive illumination. The potential for applications, in particular for intense light generation sources, arises from the specific device geometry and working mechanism, which allows to better control charge carriers injection and to limit the destructive interaction of the light-emitting excitons with the charge carriers and the electric field in the channel. The list of applications and technologies is not intended to be limitative, but only to provide examples.

The disclosures in USSN. 60/458,847 from which this application claims priority are incorporated herein by reference.